OBSERVATION OF CN A → X AND B → X EMISSIONS IN GAS-PHASE COLLISIONS OF FAST O(^{3}P) ATOMS WITH HCN

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Studies of the reaction of fast neutral atoms with molecular targets enables ona to follow tha transition between reaction channels which are normally closed under thermal-energy conditions, but which can open at higher energies. Reported herein is a study of the reaction of fast (LAB energies of 5-25 eV) O(^{3}P) atoms with HCN undertaken to identify the channel(s) which ara active in the hyperthermal energy regime. The atomic-oxygen source, target region, and spectrometer system ware the same as thet used previously in studies' of the gaseous targets H_2O, CO_2, and N_2H_4. Shown in Fig. 1 ara spectra of the CN A→X and B→X emission systems resulting from the collisions of O and HCN. Also shown is a simulation of the A→X emission in terms of energy locations and Franck-Condon factors of the vibrational bands. The laboratory energy for the O + HCN collision system was 20.0 eV, corresponding to a CM energy of 12.6 eV. The B→X system in Fig. 1 is approximately two orders of magnitude more intense than the A→X system. It is shown in more detail in Fig. 2 at a LAB energy of 10.6 eV (6.7 eV CM). Here, one has contributions from three main sequences: Δv = -t 1 centered at 358 nm, Av=O at 387 nm, and Δv = -1 at 417 nm. In addition, a nonlocal thermodynamic equilibrium (NLTE) code[2] was used to characterize the emitting B state in terms of a separate vibrational TV and rotational T, temperature. All important vibrational bands up to v'= v' = 9 were included, as wall as rotational states in each v', v" level whose rotational energy did not exceed 2.5 eV. A Boltzmann distribution of population in the B state was usad. Results are shown (solid line) for the combination T_v = 7000 K and T,= 2000 K. Agreement between experiment end simulation is within the combined uncertainties.

Central to specifying the appropriate reaction channel is the threshold energy of the channel. This in turn relies on knowledge of the energy distribution of the O(^{3}P) beam. This was obtained from the distribution of the O^- (2P) ions as measured using the retarding-potential difference method *in situ*. With the monochromator wavelength fixed at 387 nm the emission intensity was monitored as a function of O(^{3}P) energy. Results of this measurement are shown in Fig. 3. By unfolding of the O(^{3}P) energy distribution one obtains an energy threshold of 7.4 ±0.8 eV (LAB) or 4.6 ± 0.5 eV (CM). This is consistent with the reaction channel O(^{3}P) + HCN (X) → OH($X^2\Pi_i$) + CN($B^2\Sigma^+$). From the enthalpies of reaction, one calculates tha energy required for this reaction to be 4.10 eV (CM) or 6.53 eV (LAB).

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References

1. O.J. Orient, K.E. Martus, A. Chutjian and E. Murad, J. Chem. Phys. 97,4111 (1992).

2. 1.S. Bernstein, private communication.

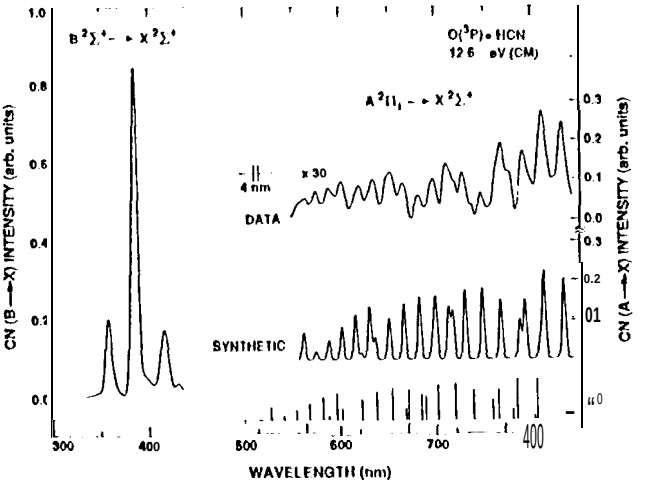

Fig. 1. *Spectra* of the CN A→X and B→X emissions.

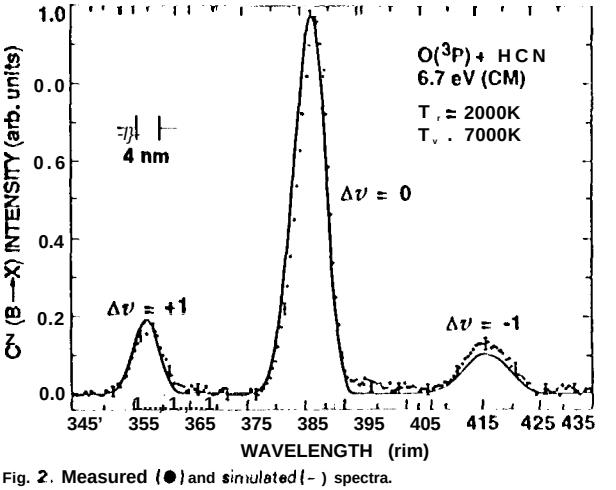

Fig. 2. Measured (●) and simulated (-) spectra.

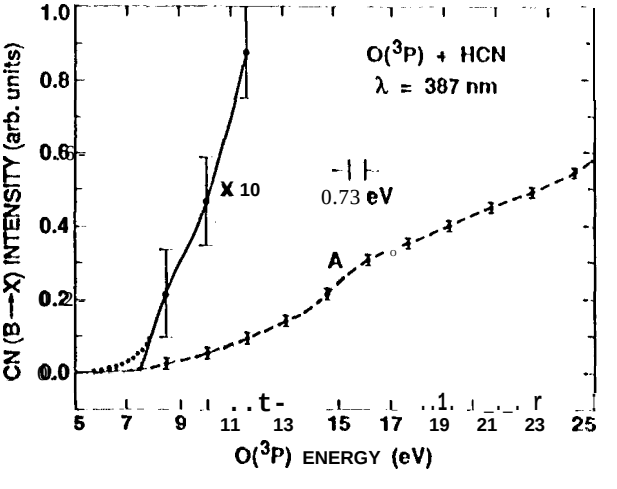

Fig. 3. Excitation function of the B→ X emission at 387 nm.